Fluorescence Spectra of Europium (III) Phthalate and Naphthalate and of Samarium (III), Europium (III), Terbium (III) and Dysprosium (III) Dipyridyl Complexes

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The line emission spectra were measured at 300 °K and 78 °K in solid samples of europium(III) phthalate and naphthalate and in the α,α′-dipyridyl complexes $Sm\,dip_2\,Cl_3, 2\,H_2O$; $Eu\,dip_2\,Cl_3, 2\,H_2O$; $Tb\,dip_2(NO_3)_3$ and $Dy\,dip_2(NO_3)_3, H_2O$. The gadolinium(III) compound $Gd\,dip_2\,Cl_3, 2\,H_2O$ shows a typical Van Uitert effect of energy transfer from the main constituent to Eu(III) and Tb(III) present in the concentration range 0.01—0.1 mole %. The methanolic solution of Gd(III) does not exhibit such energy transfer, whereas $Eu\,dip_2^{+3}$ and aqueous solutions, probably of $Eu\,phthal_2^-$ and $Eu\,naphthal_2^-$, fluoresce strongly at room temperature. However, the latter solution tends slowly to deposit crystalline salts.

Weissman [1] discovered that a number of europium(III) chelates in crystalline form or in benzene solution fluoresce by a particular mechanism: the aromatic part of the ligands absorbs visible or ultraviolet light in broad and strong absorption bands, and a part of the energy is re-emitted in narrow spectral lines. These lines are due to transitions in the central atom Eu(III) from the excited levels $^5D_1$ and $^5D_0$ to the groundstate $^7F_0$ and the adjacent excited levels $^7F_1$ and $^7F_2$ of the partly filled shell $4f^6$. These excited levels have been identified in the aqua salts and correspond to extremely weak absorption bands [2, 3], which are intensified in case of Eu(III) dialkyldithiocarbamates [4] because of the borrowing of intensity from the electron transfer band. Crosby, Whan and Alire [5, 6] observed this line fluorescence from a large number of lanthanide complexes, particularly of β-diketonates. It is generally found that the central ions closest to the half-filled shell Gd(III) such as Sm(III), Eu(III), Tb(III) and Dy(III), are most liable to fluoresce giving line spectra. On the contrary, complexes of La(III) and Lu(III) containing an empty or a filled 4f shell only show broad-band fluorescence (from excited singlet levels of the ligand) or phosphorescence (at low temperature, from triplet levels). However, if central ions such as Nd(III), Ho(III), or Er(III) were to fluoresce, the emission lines would probably occur in the infra-red. The situation for Gd(III) is exceptional, since its first excited states are in the ultraviolet, at 32 000 cm^{-1}, at a higher wavenumber than the broad absorption bands of most heterocyclic ligands.

Recently, this energy transfer from ligands to line-emitting lanthanides has caused considerable technological interest, since such complexes might permit the preparation of amorphous transparent (plastics) or liquid lasers [7] which have certain advantages over the crystalline materials (ruby or gallium arsenide) or gaseous mixtures currently applied. Actually, a great number of reports have appeared on the salicylaldehydate [1, 8] $Eu(OC_6H_4CHO)_3$ and on various Eu(III) β-diketonates [9—14] among which the benzoylacetonate and the symmetric dibenzoylmethide seem to be the most popular. However, it is worth noting that the β-diketonates are not octahedral, as is the case with d group innercomplexes [15]. Though it was previously believed that they were normal anhydrous, monomeric com-

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pounds [16] they retain tenaciously one or two molecules of water or solvent [17] or one mole of protonated ligand [17a] and actually have a very low symmetry. This is one among several reasons why we attempted to find other fluorescent lanthanide complexes. Though energy-transfer can occur across a certain distance [a most striking example being $C_{10}H_7(CH_2)_nC_{14}H_9$ where light quanta absorbed in the naphthalene chromophore produce fluorescence in the anthracene part [18]] the most efficient energy-transfer undoubtedly occurs when the distance is as small as possible.

Carboxylic Complexes

With the previous considerations in mind, we made a series of qualitative experiments, looking with a pocket spectroscope for line emission from ethanol glasses at liquid nitrogen and slightly higher temperature. As expected, no line emission is observed when pyrene, anthracene, acridine or quinine in its acid form, fluoresce in the presence of Eu(III); we would not expect the formation of complexes having Eu(III) in sufficiently close contact with the molecules capable to fluoresce. The fluoresceinate of Eu(III) only gives a broad green band at room temperature but gives line emission in liquid nitrogen. The eosinate only produced a broad yellow band under these conditions. The o-coumarate, the umbelliferonate, the anthranilate and even the β-methyl-umbelliferone (7-hydroxy-4-methylcoumarin which has a phenolic group at the seventh position) gave a mixture of broad blue bands and red lines. It is clear that the best choice is an aromatic hydrocarbon having carboxyl or hydroxyl (phenolic) groups directly attached to the ring system. Actually, we are in the near future going to investigate pyrene- and diphenyl-carboxylates. We already have certain results for phthalates and 1,8-naphthalates. The complex formation of these bidentate ligands is to be discussed soon [19]; the aqueous solution containing two or more moles of the anions phthal^{--} = $C_6H_4(COO)_2^{--}$ and naphthal^{--} = $C_{10}H_8(COO)_2^{--}$ per mole of Eu(III) forms an anion, presumably Eu phthal$_2(H_2O)_x^-$ and Eu naphthal$_2(H_2O)_x^-$. At moderate Eu(III) concentrations, 0.01 – 0.03 M, naphthalate solutions slowly deposit crystalline precipitates comparable to the nearly-insoluble hydrated oxalate. The solution containing four moles of naphthal^{--}/Eu(III) keeps for several days and gives a bright pink line emission at room temperature. We shall discuss here only the fluorescence of solid Eu(III) phthalate and naphthalate. Details of the fluorescence spectra are given in Table 1. The analogous terbium(III) compounds fluoresce green and emit several spectral lines, as usual for Tb(III) where the emission [20] goes from $^5D_4$ to the ground-state $^7F_6$ and the adjacent levels $^7F_5$, $^7F_4$, ... of $4f^8$ (see Table 2).

Dipyridyl Complexes

It is usually assumed that the lanthanides are so extreme CHATT–AHRLAND type A-central ions [21] that only oxygen-containing ligands form strong complexes. Actually, the three heavy halides form very weak complexes in water, though stronger in ethanol [4, 22], and the A-character is even more pronounced in Pr(III) than in Yb(III) [4]. However, the heterocyclic diimines phen (= o-phenanthroline) and dip (= α,α'-dipyridyl) seem to be exceptional in this respect. The reason why these ligands form stable complexes containing lanthanide-nitrogen bonds is partly due to the fact that the free ligands are far weaker bases than aliphatic amines and so have less tendency to precipitate basic salts or hydroxides, and partly due to possible steric effects. Thus, KONONENKO and POLUEKTOV [23] reported complexes such as Nd phen$_2^{+3}$ and Er phen$_2^{+3}$ and HART and LAMING [24] mentioned M phen$_3^{+3}$. Our evidence [25] rather points in the direction of solvated M dip$_2^{+3}$. The chlorides studied here, Sm dip$_2$Cl$_3$, 2 H$_2$O; Eu dip$_2$Cl$_3$, 2 H$_2$O and Gd dip$_2$Cl$_3$, 2 H$_2$O may contain as well M – OH$_2$ as M – Cl bonds (cf. GdCl$_3$,

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	λ	2.9	2.0	1.5	1.0	0.75	0.5	0.375	0.25
Eu(III)phthalate[b], 300°K	614	—	—	4.2	—	2.66	—	—	—
	590	—	—	2.1	—	—	—	—	—
Eu(III)phthalate, 78°K	614	—	—	6.5	—	4.8	—	—	—
	590	—	—	4.3	—	2.7	—	—	—
Eu(III)naphthalate[c] 300°K	—	—	—	—	—	—	—	—	—
	618.5	*	—	*	—	*	—	7.5	—
	614.5	—	—	59	—	42	—	27	—
	592	—	—	24	—	14	—	6.9	—
	589.5	—	—	*	—	*	—	—	—
	580	*	—	2.5	—	1.4	—	6.5	—
Eu(III)naphthalate, 78°K	666?	0.5	—	—	—	—	—	—	—
	653?	0.6	—	—	—	—	—	—	—
	619.7	>30	—	—	—	*	—	14	8.7
	616.5	*	—	—	—	*	—	*	15
	615.2	>30	—	—	—	80	—	59	34
	612.8	>30	—	—	—	*	—	*	6.7
	595.1	>30	—	—	—	*	—	10	5.4
	592.4	>30	50	—	—	27	—	16	10.5
	590.0	>30	—	—	—	*	—	15	9.0
	580.0	*	—	—	—	3.4	—	—	—
Eu dip_2Cl_3, $2H_2O$, 300°K	698	—	—	2.7	2.0	—	—	—	—
	654	—	—	1.0	—	—	—	—	—
	618.5	—	—	*	*	—	30	—	14
	615.5	—	—	>70	89	—	63	—	20
	613.0	—	—	*	*	—	—	—	45
	593	—	—	>70	*	—	} 87	—	31
	592	—	—	>70	>100	—	}	—	50
	579.5	—	—	11	9.3	—	—	—	8.3
	555.5	—	—	2.5	2.0	—	—	—	—
	536	—	—	4.0	3.4	—	2.4	—	—
Eu dip_2Cl_3, $2H_2O$, 78°K	699	—	—	1.8	1.4	—	—	—	—
	619.2	—	—	*	25	—	—	—	12
	616.2	—	—	68	59	—	—	—	14
	613.5	—	—	*	*	—	—	—	42
	593.5	—	—	*	*	—	—	—	26
	592.0	—	—	>80	89	—	—	—	50
	580.5	—	—	5.2	4.1	—	—	—	—
	555.5	—	—	2.1	1.8	—	—	—	—
	536	—	—	2	3.1	—	—	—	—
Tb $dip_2(NO_3)_3$, 300°K	622	—	—	2.2	—	1.3	—	—	—
	584.5	—	—	18	—	10	—	6.8	—
	547	—	—	>70	—	65	—	40	—
	542	—	—	>70	—	81	—	56	—
	490.5	—	—	>70	—	54	—	40	—
Gd dip_2Cl_3, $2H_2O$, 300°K	613	—	—	2.3	2.0	—	—	—	—
	592	—	—	3.3	2.8	—	—	—	—
Gd dip_2Cl_3, $2H_2O$, 78°K	614	—	—	1.7	1.4	—	—	—	—
	592	—	—	3.6[a]	2.3	—	—	—	—
	587	—	—	3.0[a]	2.1	—	—	—	—
	545.5	—	—	19[a]	13[a]	—	—	—	—
	489.5	—	—	14[a]	8.3[a]	—	—	—	—
Sm dip_2Cl_3, $2H_2O$, 300°K	598	—	2.5[a]	—	1.6	—	—	—	—
	561	—	2.2[a]	—	1.2	—	—	—	—
Sm dip_2Cl_3, $2H_2O$, 78°K	600.5	—	4.0[a]	—	—	—	—	—	—
	564	—	2.6[a]	—	—	—	—	—	—
Dy $dip_2(NO_3)_3$, H_2O, 300°K	573	—	21[a]	—	15[a]	—	8.5	—	—
	482	—	29[a]	—	18[a]	—	9.2	—	9.4
	477	—	—	—	—	—	4.8	—	—
Dy $dip_2(NO_3)_3$, H_2O,78°K	573.5	—	—	—	81[a]	—	50	—	—
	481	—	—	—	>100[a]	—	74	—	—

Table 1. Details of fluorescence spectra. The first column gives the wavelength λ of the lines in mμ. The following columns give the values of the intensity ratios $(10)^{2-D/S}$ as a function of slit-widths (See Text). Asterisks mark the components that were not resolved at the slit-width considered.

[a] The line intensity includes the contribution from an emitted continuum. [b, c] The solid chelates have the formulae $Na[Eu(C_8H_4O_4)_2]$, $4\,H_2O$ [b] and $Na[Eu(C_{12}H_6O_4)_2]$, $4\,H_2O$ [c] respectively.

	λ	σ	assignment	σ_{exc}
Sm dip_2Cl_3, $2H_2O$	599	16690	$^4X \rightarrow {}^6H_{7/2}$	1100
	562	17790	$^4X \rightarrow {}^6H_{5/2}$	0
Eu(III)phthalate[a]	614	16290	$^5D_0 \rightarrow {}^7F_2$	~ 960
	590	16950	$^5D_0 \rightarrow {}^7F_1$	~ 300
Eu(III)naphthalate[a]	666 ?	15015	$^5D_0 \rightarrow {}^7F_3$	2225
	653 ?	15315		1925
	619.7	16140	$^5D_0 \rightarrow {}^7F_2$	1100
	615.2	16255		985
	612.8	16320		920
	595.1	16800	$^5D_0 \rightarrow {}^7F_1$	440
	592.4	16880		360
	590.0	16950		290
	580.0	17240	$^5D_0 \rightarrow {}^7F_0$	0
Eu dip_2Cl_3, $2H_2O$	699	14300	$^5D_0 \rightarrow {}^7F_4$	~ 2930
	654	15290	$^5D_0 \rightarrow {}^7F_3$	~ 1940
	619.2	16150	$^5D_0 \rightarrow {}^7F_2$	1080
	616.2	16230		1000
	613.5	16300		930
	593.5	16850	$^5D_0 \rightarrow {}^7F_1$	380
	592.0	16890		340
	580.5	17230	$^5D_0 \rightarrow {}^7F_0$	0
	555.5	18000	$^5D_1 \rightarrow {}^7F_2$	—
	536	18660	$^5D_1 \rightarrow {}^7F_1$	—
	527 ?	18980 ?	$^5D_1 \rightarrow {}^7F_0$	—
Tb $dip_2(NO_3)_3$	622	16080	$^5D_4 \rightarrow {}^7F_3$	4310
	584.5	17110	$^5D_4 \rightarrow {}^7F_4$	3280
	547	18280	$^5D_4 \rightarrow {}^7F_5$	2110
	542	18450		1940
	490.5	20390	$^5D_4 \rightarrow {}^7F_6$	0
Dy $dip_2(NO_3)_3$, H_2O	573.5	17440	$^4X \rightarrow {}^6H_{13/2}$	3550
	481	20790	$^4X \rightarrow {}^6H_{15/2}$	0

Table 2. Wavelength λ in mμ, wavenumber σ in cm^{-1} and assignment of excited and terminal levels of fluorescence lines observed. The wavenumber σ_{exc} indicates the height of the latter level above the ground level.

[a] For the formula see Table 1.

$6H_2O$ containing [26] the chromophore $Gd(III)Cl_2O_6$), whereas the nitrates Tb $dip_2(NO_3)_3$ and Dy $dip_2(NO_3)_3$ H_2O definitely [25] contain coordinated oxygen atoms from nitrate groups. The occurrence of fluorescence at room temperature in the complexes of Sm(III) and Dy(III) is a rather rare phenomenon. Samarium(III)tris(theonyltrifluoroacetonate) [27] fluoresces at 645, 598 and 562 mμ at room temperature.

We were surprised to observe pink line-emission from Gd dip_2Cl_3, $2H_2O$ made from better than 99.9% Gd_2O_3. The fluorescence spectrum clearly shows Eu(III) and, at 78 °K, also Tb(III) lines (Table 1). Though these constituents are estimated to be present only in the concentration range 0.01 to 0.05 molar %, the relative fluorescence intensity (evaluated according to the considerations mentioned in the experimental section) corresponds to about 2% Eu(III) at 300 °K and 3% Eu(III) at 78 °K. At room temperature, no Tb(III) emission is perceptible from the gadolinium complex (i. e. less than 0.4% Tb(III) intensity) whereas at 78 °K, the Tb(III) lines are as intense as if the compound contained 20 molar % terbium. This phenomenon can be ascribed to the energy transfer from dipyridyl molecules adjacent to gadolinium central atoms to the "energy trap" predominantly consisting of Tb(III) at low temperature and Eu(III) at room temperature. Similar effects have been extensively studied by Van Uitert and his collaborators [28–30] on compounds such as $Na_xCa_{1-2x}M_xWO_4$ or the hexa(antipyrine) iodides $[M(C_{11}H_{12}N_2O)_6]I_3$. It is remarkable to what extent very small amounts of

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Eu(III) and Tb(III) may take over the energy absorbed in nearly pure Gd(III) compounds and then emit their characteristic lines. The "VAN UITERT" effect does not usually occur in solutions, and actually, our Gd dip_2Cl_3, $2\,H_2O$ shows no fluorescence in methanolic solution.

Discussion

It is seen from Table 1 that usually [with the exception of the VAN UITERT effect for Tb(III) in Gd dip_2Cl_3, $2\,H_2O$ and in the case of Dy $dip_2(NO_3)_3$, H_2O] there is somewhat larger fluorescence intensity at 78 °K than at 300 °K. Since no spectacular increase of intensity occurs at low temperature, we conclude that quenching of fluorescence due to vibrational effects is not the main reason determining the quantum yields for fluorescence in our compounds. The main factor seems to be a "bottleneck" in the energy transfer from the aromatic ligands to the 4f shell. We did not attempt to measure absolute quantum yields, and as we discuss in the next section, there are various reasons why the intensities in Table 1 have only a qualitative value. However, in order to have a comparison spectrum, we recorded the fluorescence of uranyl acetate $UO_2(O_2CCH_3)_2$, $2\,H_2O$ under the same conditions in which the fluorescence of the rare-earth ions was studied. Table 3

λ	σ	0.19 mm	0.095 mm
618	16180	—	—
587	17040	—	—
557.5	17940	32	17
532	18800	130	60
509.2	19640	275	132
488	20490	120	54

Table 3. Room temperature fluorescence spectrum of uranyl acetate. Notation as in Table 1.

shows the characteristic vibrational structure of equidistant bands spaced 860 cm^{-1} apart (the symmetric stretching frequency [31] of the electronic groundstate of UO_2^{++} being 860 cm^{-1} whereas the first absorption system of UO_2^{++} shows [32] intervals around 710 cm^{-1}). From a comparison of Table 1 and 3 we tentatively conclude that the most intense fluorescence lines of our Eu(III), Tb(III) and Dy(III) complexes are some five times weaker than those of UO_2^{++}. However, the crystal size and various other factors make it difficult to compare the actual quantum yields that way. Recently, a quantum yield 0.56 ± 0.08 has been reported for the 612.2 mμ fluorescence of an acetone solution of Eu(III) tris(theonyltrifluoroacetonate) [33].

It was argued by SAMELSON and LEMPICKI [12] that the half-lives of about 0.5 millisecond measured for Eu(III) tris(β-diketonates) at 77 °K as well as at 300 °K (though the fluorescence yield may be much smaller in the latter case) approach the actual radiative half-life of the excited state $^5D_0$ (the value is only 3 microseconds [9] for $^5D_1$). The corresponding value for $^5D_0$ of Eu(III) in CdF_2 where the main intensity is concentrated in the transition to $^7F_1$ seems to be 10 milliseconds [34]. The level $^5D_4$ in Tb(III) has a half-life of some 5 milliseconds in hexa-antipyrine iodide [35] whereas it is about 1 millisecond in the anthranilate [10] and the acetylacetonate [11].

It is well known that the fluorescence from a given excited level very frequently goes predominantly to the groundstate and hardly at all to excited levels of considerable energy. In other words, this might be described as a dependence of the fluorescence intensity on a high power of the wavenumber of the emitted light. Eu(III) is an exception because the transitions from $^5D_0$ and $^5D_1$ to $^7F_0$ are particularly forbidden, and actually, it is doubtful whether we observe the latter transition in Eu dip_2Cl_3, $2\,H_2O$ (Table 1, 2). On the other hand it is instructive to note that the transition $^4X \rightarrow {}^6H_{11/2}$ predicted [36] at 15 100 cm^{-1} for Dy(III) has not been observed.

It would have been observed if it had produced a signal on the Cary spectrophotometer at least 0.005 times that of the transition $^4X \rightarrow {}^6H_{13/2}$.

Table 2 shows that the distribution of J-levels of the various $4f^q$-configurations is exactly as expected from the study of other lanthanide compounds [36]. We have not observed a particularly strong splitting due to "ligand field" effects (i. e. the σ-anti-bonding effect of the ligands on the 4f shell [36, 37]). Thus,

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$^7F_2$ has the width 180 cm^{-1} in Eu(III) naphthalate and 150 cm^{-1} in Eu dip_2Cl_3, $2\,H_2O$, whereas in cubic $Eu_{0.14}Th_{0.86}O_{1.93}$ the width[38] of $^7F_2$ is 430 cm^{-1} and $^7F_1$ does not split in agreement with the explanation by group-theory. Incidentally, the splitting of $^7F_1$ in three components in the Eu(III) naphthalate complex shows a rather low micro-symmetry (if a three-fold axis was present, as in [39] $LaCl_3$ or a four-fold axis, only two components would be observed). This observed splitting may be compared to that of the tris(dibenzoylmethide) [14] having $^7F_2$ components at 617.4, 615.2, and 612.1 mμ with a total width of 240 cm^{-1}.

We are not going to investigate whether our compounds have any potential use as lasers, since this will be done by our colleague Dr. FRED HALVERSON at the American Cyanamid laboratories in Stamford, Conn. However, it is interesting that aqueous solutions at room temperature or methanolic solutions (which have the advantage of freezing sharply at $-98\,^{\circ}C$, whereas cooled ethanol becomes viscous like glycerol and cannot readily be circulated and cooled) may possibly be within the class of laser materials. It seems quite plausible that a wide variety of ligands [21] might form acceptable fluorescent Eu(III), Tb(III) and Dy(III) complexes.

Experimental

Compounds were prepared from 99.9%, or better, rare earths (American Potash, Lindsay Division, West Chicago) except certain samples of europium(III) complexes made from 99% Eu_2O_3 (the rest mainly La_2O_3) from Orquima I.Q.R.s/A, Sao Paulo. The details of preparation of dipyridyl complexes are given elsewhere [25]. The phthalates and naphthalates are precipitated from solutions, the equilibria conditions of which are discussed separately [19].

Sodium naphthalate was precipitated from the aqueous solution of Fluka naphthalic acid in 1 M NaOH with three volumes of ethanol. In this way, a brown impurity is removed and one can readily make a nearly colourless stock solution of 0.2 M Na_2 naphthalate in water.

For the qualitative experiments, the ligands for making fluorescent compounds were obtained from Fluka, Buchs, and 0.01 M ethanolic or aqueous solutions were added to varying amounts of 0.03 M europium(III) chloride in ethanol. A Mineralight short wave (253.7 mμ) or long wave (366 mμ) ultraviolet lamp with black filter was used as light source. The emission spectra were observed with a Schmidt-Haensch "Longo II" spectroscope.

Fluorescence spectra were measured on a Cary 14 spectrophotometer. The geometry of the instrument was suitably modified for detecting and recording fluorescent radiation from the samples. For low-temperature work the samples were mounted on the "cold finger" of a cryostat. The spectrophotometer was used as a single-beam instrument. In order to have some way to estimate the fluorescence intensity, we tried to keep the geometry of the system and the sensitivity of the detecting-recording sections unaltered. The only variable condition was the entrance slit-width of the Cary. The optical-density measuring slide-wire was used. The intensities given in Table 1 are derived from the convention that the optical density reading on the chart at $D=0$ corresponds to the intensity 100; $D=1$ to 10; $D=1.5$ to 3.1 and $D=2$ to 1. We then divided these intensities by s, the slit-width in mm, in order to get comparable values in Table 1. The samples were excited by 3660 Å radiation from an Hanovia fluorescent lamp model 11.

However, it is seen that the light intensity going through our device rather is proportional to the square of the slit-width which seems to be an inherent feature in the spectrophotometer. If the half-width of the lines emitted were comparable to the instrumental bandwidth for a given opening of the slit, nearly invariant values of $(10)^{2-D}$ would be expected. Since we are using the apparatus as a spectral-energy recorder, we ought to correct for the varying sensitivity of the photocells. Such ratios are far from being constant. Hence comparison between intensity of emitted lines in various compounds using the data of Table 1 should only be restricted to values corresponding to the same spectral region and the same slit-width.

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